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Technique for Measuring Reduced Forms of Sulfur in Ambient Air

University of South Florida
Tampa

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Environmental Sciences Research Lab
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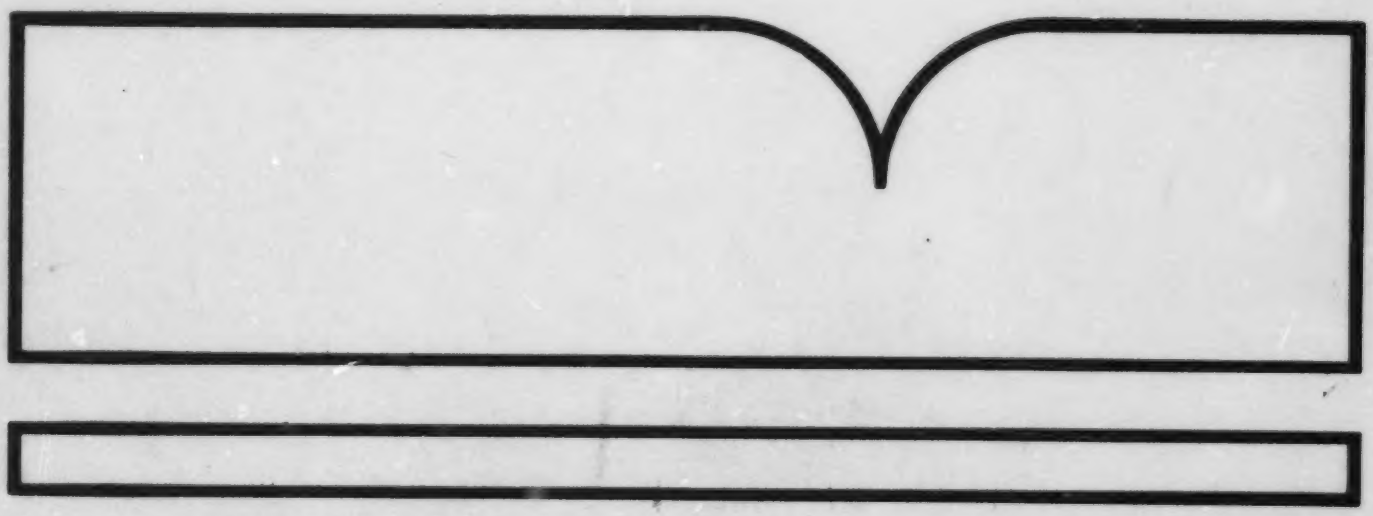

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16. ABSTRACT

A new technique for measuring low concentrations of volatile sulfur compounds in ambient air is discussed. The technique consists of preconcentration of sulfur compounds by chemisorption on gold metal coated sand or gold foil surfaces followed by thermal desorption, separation, and detection by flame photometry. Breakthrough capacities are on the order of 1 microgram total sulfur compounds. The unique aspect of this research is the derivatization of thiol type compounds, principally H_2S and CH_3SH, by ethyl iodide for partial separation of H_2S, DMS, SO_2, COS, and CH_3SH. Best suited for the 0.01 - 5 ppb range, the technique has been used to detect trace sulfur compound concentrations as low as 0.001 ppb by volume with 100L and larger sample volumes. Sample size detection limits depend upon the type of flame photometric detector used but are generally in the 0.1 ng range. Repeatability of measurements is $\pm$5-8% relative standard deviation. Accuracy depends upon the compound. DMS and SO_2 are detected as individual compounds. H_2S, CS_2 and COS are detected as a single compound on gold foil. Methylmercaptan and dimethyldisulfide appear as a single compound. Field studies at two sites, Cedar Island N. C. and Prairie View, Texas, have demonstrated that the technique is practical for field use and for determining vertical profiles up to 10 meters above ground level. Hydrogen sulfide, dimethylsulfide, sulfur dioxide and carbonylsulfide were the principal reduced forms of sulfur detected at these sites.

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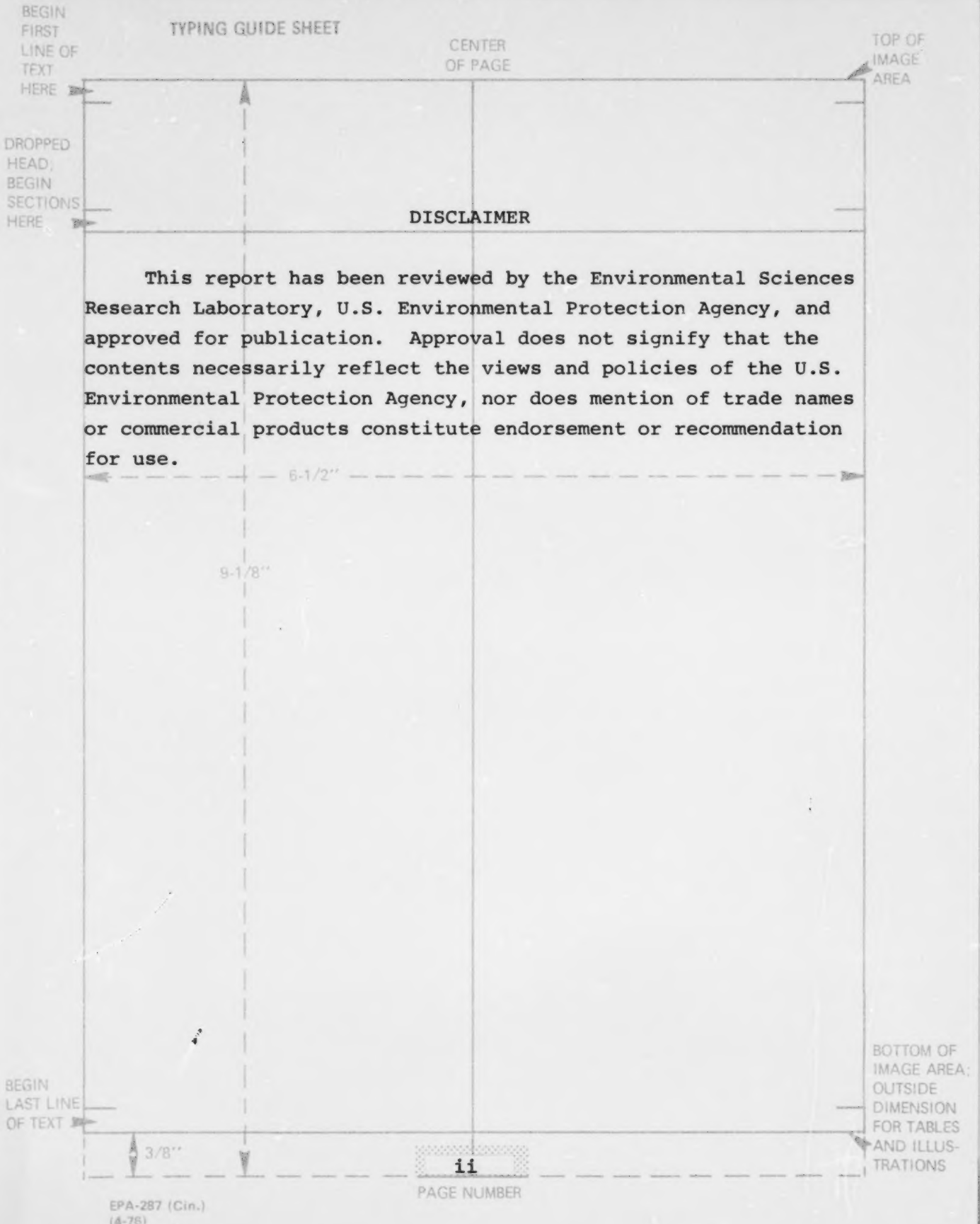
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ABSTRACT

This report explains the use of a new technique for the measurement of low concentrations of volatile sulfur compounds in ambient air. The technique consists of preconcentration of sulfur compounds by chemisorption on gold metal coated sand or gold foil surfaces followed by thermal desorption, separation and detection by flame photometry. Breakthrough capacities are on the order of 1 microgram total sulfur compounds. The unique aspect of this research is the derivatization of thiol type compounds, principally H_2S and CH_3SH by ethyl iodide leading to partial separation of H_2S, DMS, SO_2, COS, and CH_3SH. Best suited for the 0.01 - 5ppb range, the technique has been used to detect trace sulfur compound concentrations as low as 0.001 ppb by volume with 100L and larger sample volumes. Detection limits depend upon both the type of flame photometric detector used and the compound detected and are generally in the 0.1 ng range. Repeatability of measurements is ±5-8% relative standard deviation. Accuracy depends upon the compound. DMS and SO_2 are detected as individual compounds. H_2S, CS_2 and COS are detected as a single compound on gold foil. Methylmercaptan and dimethyldisulfide appear as a single compound. Field studies at two sites, Cedar Island, N.C. and Prairie View, Texas have demonstrated that the technique is practical for field use. Hydrogen sulfide, dimethylsulfide, sulfur dioxide and carbonyl sulfide were the principal reduced forms of sulfur detected at these sites.

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SECTION 1

INTRODUCTION

The most widely used commercial instrumentation for sulfur compounds in air employs the methods of Stevens, Mulik, O'Keeffe and Krost (1) and Stevens, O'Keeffe and Ortman (2) or modifications and improvements thereof. These methods are readily applicable for direct sulfur analyses at or above 1 ppb, and capable of separating several sulfur compounds in air.

In earlier work (3) on preconcentration and analysis of air for reduced forms of sulfur it was found that ambient concentrations of H_2S, $(CH_3)_2S$ and CH_3SH compounds in non-polluted locations are in the 0.01 - 1 ppb range. This is also the experience of others (4) (5) doing similar work on ambient sulfur-in-air analyses. None of these methods were capable of avoiding oxidation losses of H_2S and CH_3SH and SO_2 was somewhat of an interference.

Consequently, this study was undertaken to further explore and improve the gold surface adsorption approach (3). In the improved method reported here reduced sulfur compounds are adsorbed onto gold metal coated silica sand or gold foil. Chemisorbed and preconcentrated sulfur compounds are derivatized to alkyl sulfides by ethyl iodide, desorbed by heating, separated on a short column and then detected by means of a flame photometric detector.

Preconcentration by means of gold coated silica sand was developed first, studied for interferences and used in the two field studies reported here. Nitrogen dioxide and ozone interfere if sample volumes over 20-30 liters are used or if present in elevated concentrations. These interferants are

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removed by use of a sodium carbonate filter.

The method was used in field studies at Cedar Island, North Carolina and at Prairie View, Texas where H_2S, DMS, SO_2 and COS were the major reduced compounds of sulfur detected. Diurnal variations and vertical profiles of sulfur compounds are reported.

After the field studies further methods development was carried out including investigation of gold foil preconcentration and investigation of high molecular weight secondary amines for COS and CS_2 preconcentration. Gold foil preconcentration was found to be less sensitive to oxidation than gold coated silica. The use of high molecular weight amines for COS and CS_2 preconcentration was not successful.

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SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The preconcentration of reduced compounds of sulfur on gold metal surfaces has been studied, improved and applied in field analyses. The major improvement made was the addition of a derivatization step in the procedure.

The derivatization of thiol compounds by ethyl iodide eliminates sulfur dioxide and sulfate interferences in preconcentration prior to desorption and analysis. Sample volumes up to 50 liters can be preconcentrated with minimal interference from ozone or nitrogen oxides present in air so long as sodium carbonate scrubbers are employed. Carbonyl sulfide is collected and identified separately on gold coated sand but carbon disulfide is derivatized and not distinguished from hydrogen sulfide. On gold foil H_2S, CS_2 and COS all appear as the same derivative. Within these limitations the method is useful for preconcentrating and determining H_2S, $(CH_3)_2S$, COS, CH_3SH and CH_3-S-S-CH_3 at concentrations as low as 1 ppt.

Gold foil preconcentrators appear to have the advantage of easier adaptability to automated use than the gold coated sand tubes.

Polymeric secondary amines of several types preferentially absorb COS and CS_2 while not absorbing H_2S. Unfortunately, thermal desorption of the COS and CS_2 is incomplete and the approach was not successful.

Field use of the method at Cedar Island, N.C. and Prairie View, Texas indicated that COS, H_2S, SO_2 and DMS exhibit a diurnal variation with increased production in salt marshes during the day. These sulfur compounds are produced in the ground and

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diffuse into ambient air.

Although suitable for qualitative examination of vertical profiles, the sampling time required and precision of the method are probably not sufficient for accurate calculation of dry deposition rates.

Recommended further study of the analytical approach includes modification to selectively separate and determine COS and CS_2. To this end, study of diffusion-discriminating hollow metal coated tubes is suggested. Further suggested studies would be gas to particle conversion at the ground level in air and further verification of the diurnal variation at locations other than over salt marshes.

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SECTION 3

ANALYTICAL PROCEDURES

GENERAL

The general analysis approach was to preconcentrate gaseous sulfur compounds from air onto gold coated silica contained in small sampling tubes. Particles were removed by filters. Sulfur compounds once separated, were detected by means of a flame photometric detector.

SAMPLING

Air sampling was accomplished using the adsorption tube design shown in Figure 1. White beach sand was boiled with aqua-regia to remove carbonates and traces of iron and copper, water washed, and then sieved to 40-60 mesh size. The sand was gold coated by first mixing the sand with a solution of auric chloride. Sand was then taken to dryness with stirring on a hot plate. This was followed by hydrogen reduction at elevated temperature. Enough gold chloride was used to give a 5%-10% gold coating by weight on the sand. The tubes were segmented as shown in Figure 1 to prevent cracking of the quartz because of thermal expansion of the sand during heating in the analysis procedure.

Flow rates through the filter and adsorption tubes were determined for each set of sampling pump, tube and filter used in air sampling. A study of flow rates for the arrangement showed that the Millipore type FA particulate filters had little effect on air flow restriction compared to the sampling tubes. All 25 particulate filters prepared for the field studies were the same in this respect.

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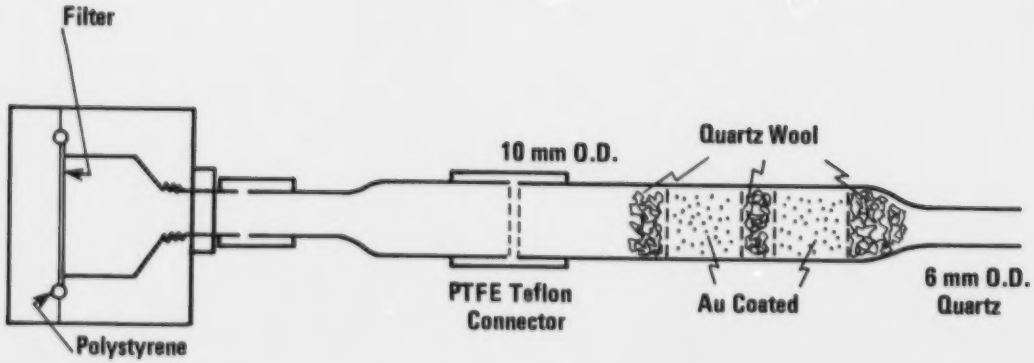

Figure 1. Preconcentration Tube Design

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Thirty tubes of the design shown in Figure 1 exhibited the same pressure drop under sampling operation within ± 7% r.s.d. When used with Neptune Dyna-Pumps, model 4K, flow rates were 2.4 L $min.^{-1}$. In vertical sampling studies two sampling tubes were used per pump with flow rates averaging 1.6 L $min.^{-1}$.

Air sampling was generally done at 2 meters above the ground. In certain instances sampling was done with towers at several distances above the ground at generally, 10, 5, 2, 1, 0.5 and 0.2 meters. Samplers were mounted on towers constructed of TV antenna material, attached to a wooden base, and supported by guide ropes. The ropes were secured to metal stakes driven into the ground. Two persons could easily raise and lower the towers. Sample tube holding brackets were attached to the towers at the requisite heights above the ground. Tygon tubing was taped to the tower and used to provide the attachment of sampling tubes and filters to the pumps mounted at the base of the towers. Electrical switching boxes were mounted on the tower bases.

PRECONCENTRATION TUBE ANALYSIS

Preconcentration tubes adsorb SO_2, H_2S, CH_3SH, $(CH_3)_2S$, COS, and other sulfur compounds from air quantitatively at the flow rates used in sampling. These compounds are desorbed from the tubes in a two-step analysis, trapped in a short liquid nitrogen cooled U-trap, separated during the heating of the U-trap and detected by means of a flame photometric detector. Figure 2 shows the analysis apparatus arrangement.

Separation of sulfur compounds is accomplished in the U-trap part of the analysis system during heating. Small amounts of SO_2 are also separated from the other compounds in this step. When several ppb of SO_2 are present, some is adsorbed onto the quartz wool and is desorbed on heating after deactivation of the gold by ethyl iodide.

The U-trap is constructed of 6 mm o.d. borosilicate glass and is 15 inches long packed with OV-3, 15% Anakrom C-22, 40/50

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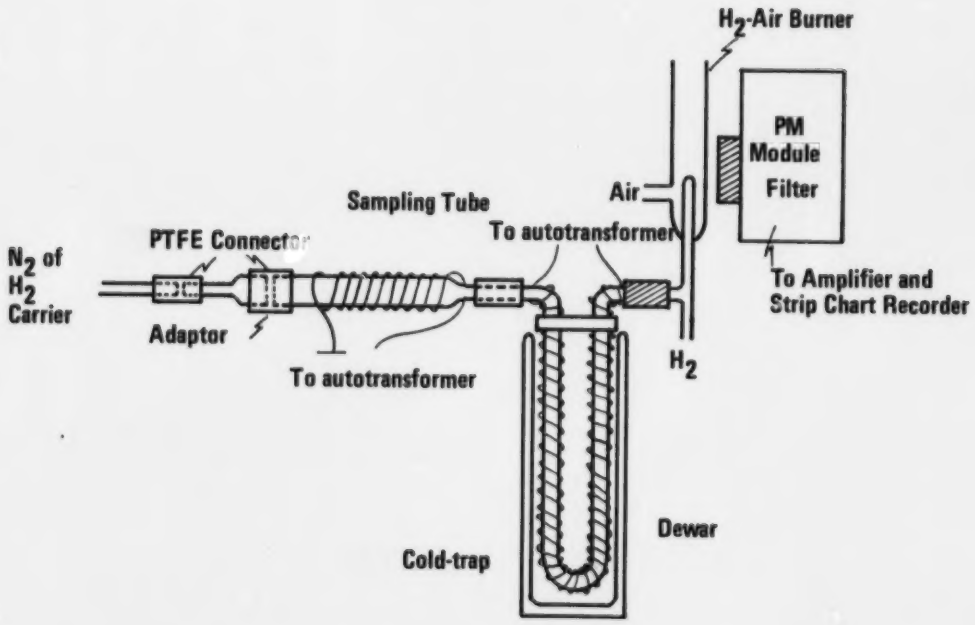

Figure 2. Analysis apparatus arrangement

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mesh (Analabs, Inc., New Haven, Conn.). Many gas chromatographic packings have been found to be reactive with H_2S and other thiols even to the extent that columns often chemisorb small amounts. Our work indicates that removal of traces of (principally) iron in the column support eliminates absorption problems. Iron is removed from the Anakrom C22 by boiling with concentrated HCl until iron tests are negative as tested with thiocyanate ion indicator or by atomic absorption analysis.

The FPD is constructed using an interference filter, quartz burner and MacPhearson Co. monochrometer. A logarithmic amplifier was used to linearize detector response to sulfur for one of the two analyzers used. Except for the logarithmatic amplifier, both analyzers were of the same design. Integrating strip chart recorders with off-scale capability were used with both analyzers.

The first desorption step involves derivatization of sulfur compounds on the preconcentration tube. Ethyl iodide vapor, 1 mL, is injected into the nitrogen carrier gas stream with the liquid nitrogen Dewar in place and passes through the preconcentration tube. It is then heated to 300-400°C for 2-4 minutes during which time several things occur. Ethyl iodide, far in excess of the sulfur present, approximately 1 mg, is adsorbed onto the gold surface and the excess is collected in the cold U-trap. Upon heating, some of the ethyl iodide converts the RSH and H_2 present to the ethyl derivatives, likely by two steps.

$$C_2H_5\ I + Au \longrightarrow AuI^- + C_2H_5^+$$

$$2\ C_2H_5^+ + H_2S \longrightarrow (C_2H_5)_2S + 2H^+$$

$$AuI^- + H^+ \longrightarrow HI \cdot Au$$

Alkylthiols are converted to the ethyl derivative by the same reaction.

$$C_2H_5I + C_4H_9SH \longrightarrow C_4H_9SC_2H_5 + HI$$

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Sulfur dioxide does not react. Carbonyl sulfide and carbon disulfide, if present and adsorbed on the gold, are also converted to diethyl sulfide (DES).

Dimethyl sulfide is also adsorbed by gold, but does not change its identity in the alkylation and analysis process. Some of the adsorbed dimethyl sulfide is desorbed during the alkylation process. This does not occur when dimethyl sulfide is adsorbed onto gold foil. Some of the dimethyl sulfide is adsorbed onto the quartz wool in the packed tubes and is displaced by the ethyl iodide alkylating reagent.

For gold coated sand tubes, COS is observed to be adsorbed onto the quartz wool part of the preconcentration tube where it is not converted in the alkylation process because it is not present on the gold surface and excess ethyl iodide takes up all of the active sites on the gold. Carbonyl sulfide is removed from the quartz wool during the first heating step and is recovered as COS in the analysis of the U-trap. Carbonyl sulfide is probably stabilized as an ammonia or amine adduct which is decomposed by heating.

The second step in analysis determines SO_2 adsorbed onto the preconcentration tubes. The carrier gas is switched to hydrogen and the U-trap is cooled. The tubes are then heated for 3 minutes to 600-700°C. Sulfur dioxide still adsorbed onto the gold is converted to H_2S which is desorbed and trapped by the U-trap. The U-trap is allowed to warm up, and H_2S is detected. A single heating period will remove all SO_2, but if some oxidation to SO_3 or H_2SO_4 has occurred, a repeat heating period is needed. Samples allowed to stand overnight before analysis appear to exhibit conversion of about half of the SO_2 to SO_3 or H_2SO_4. Hydrogen sulfide, DMS, and COS do not appear to be lost on standing overnight (12-16 hours).

Typical response curves are shown in Figures 3 and 4. These were obtained from the two field studies reported here. Note the difference in the nature of the excess ethyl iodide response. A positive ethyl iodide response is observed in more

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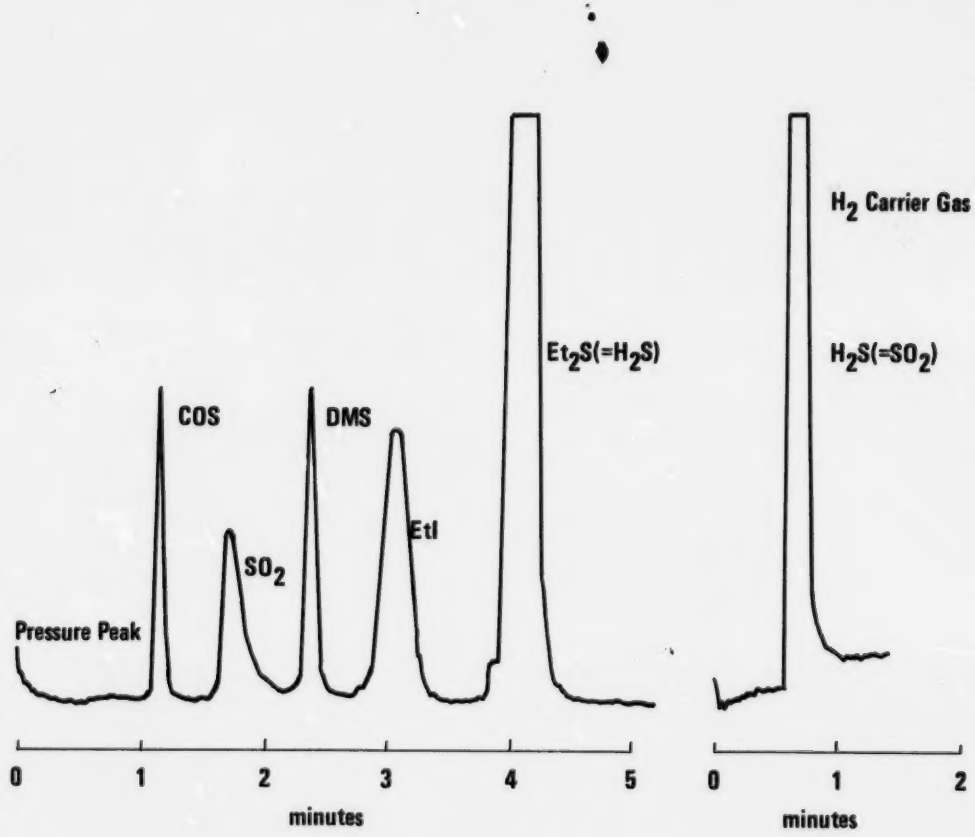

Figure 3. Analysis of preconcentrated air sample from Cedar Island, N.C.

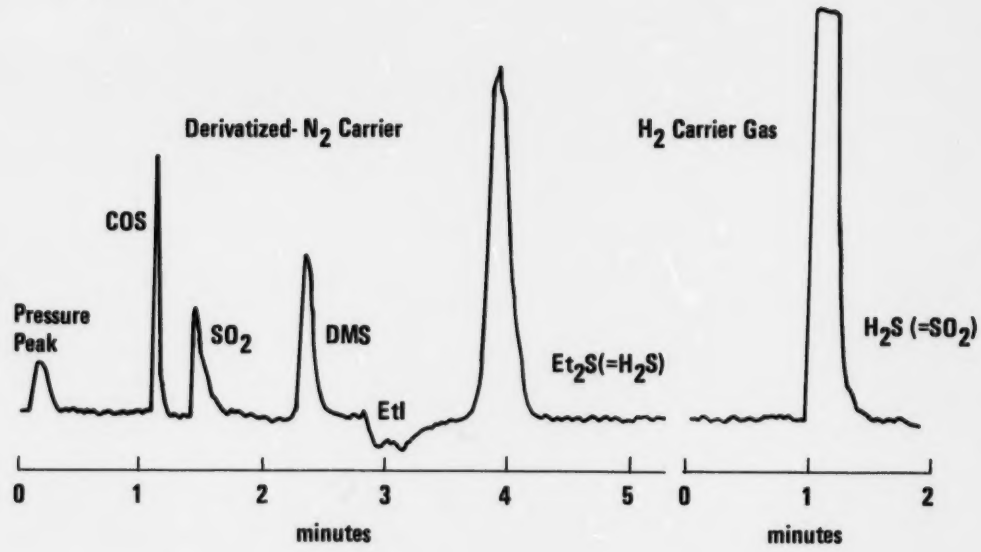

Figure 4. Analysis of preconcentrated air sample from Prairie View, TX

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air-rich flame mixtures. In more hydrogen-rich flame mixtures a quenching of the flame background is observed. The FPD used was calibrated using different flame mixtures in the two field analysis studies. A peak area integrator with 4 times off scale integration range was also used. The integrator response is not shown.

Response calibration was done at both field study locations using permeation tubes (for SO_2, H_2S, DMS) and an air mixing manifold. Permeation rates, determined gravimetrically, were corrected for temperature effects. Response curves were prepared by absorbing known amounts of the low concentrations of diffusion tube standards onto blanked preconcentration tubes followed by their analysis.

The typical reproducibility of standards on adsorption tubes has been determined from several sets of standardization experiments and was found to be ± 4.5 - 5% for DMS and H_2S, ± 8 - 10% for SO_2, all in units of relative standard deviation.

IDENTIFICATION OF COS

Identification of the first peak in the analysis (see Figures 3 and 4) of natural air samples as carbonyl sulfide was based on a number of experiments. The boiling point of the compound emerging first in the analysis had to be well below that of SO_2. It had approximately the same retention time as that of H_2S. Since H_2S had always been completely alkylated to DES in all prior experiments, it was at first thought that S_2O (however unlikely) might be the early peak observed.

The reactive suboxide S_2O was prepared and tested for its separation on the U-trap. This compound was found to decompose. It gave no peaks at the proper retention time for COS or the early peak in analyses. Large amounts of SO_2 were observed with a small peak probably indicating some S_2O present. The SO_2 comes from the reaction

$$2S_2O \longrightarrow S_3 + SO_2$$

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Attempts to produce the initial peak from SO_2, H_2S, CS_2 and mercaptans on the sampling tubes during analysis were likewise unsuccessful.

The most indicative experiments were those done with a surface pH modified U-trap column. The OV-3 on Anakrom C-22 column was first treated with methylamine vapors rendering the column somewhat basic. The retention of H_2S and COS was then noted on this column. Hydrogen sulfide was only very slowly removed from this column during the U-trap heating. Its peak was poorly defined and spread out. This is attributed to the acid-base reaction between H_2S and methylamine. Under the same conditions, COS remained as a sharp peak, detected early in the separation. It is apparent that the $CH_3NH_2 \cdot COS$ adduct is less stable than the $CH_3NH_2 \cdot H_2S$ adduct. Analyses of environmental samples exhibiting the COS peak on the usual separation column also gave the same peak on the CH_3NH_2 treated column. Addition of COS to natural samples enhanced the first peak.

A second set of experiments was carried out with a packed U-trap treated first with methylamine and then with several milliliters of HCl vapors. This "buffered" column gave a peak for both COS and H_2S. Hydrogen sulfide was later and well separated from COS. Environmental samples analyzed using this column gave only the initial, COS peak.

Short columns containing small amounts of tetraethylenepentamine, which was known to absorb COS, placed just in front of the preconcentration tubes removed the COS peak but no other sulfur compounds.

All of the above plus the indication of other workers, (6) (7) who have reported COS as present in the environment eventually brought us to the same conclusion. The initial peak is COS and the compound is present in the environment.

Results of the diurnal studies in which the variation of COS follows H_2S variation indicates that COS may be produced as a result of photosynthetic activity.

It is likely that environmental COS is associated with

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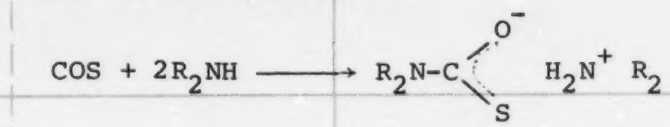
ammonia or amines since these compounds can form adducts of the type shown below. The ammonia content of air is probably well above that of COS in most locations.



These adducts account for the stability of COS in preconcentration. The adducts apparently absorb onto the quartz wool part of the preconcentration tubes. Ethyl iodide deactivates the gold tube surface in the analysis step and the COS adduct dissociates during the initial heating period to produce COS which emerges as this compound upon analysis of the U-trap.

OZONE AND NO_2 INTERFERENCES

Exposure of unprotected gold sampling tubes to 100 ppb ozone or nitrogen dioxide for 15 to 20 minutes during sampling was found to cause a 60% reduction in preconcentrated hydrogen sulfide. At lower ozone concentrations, proportionately smaller losses were observed. Of the two, ozone is likely the major interfering oxidant as it is generally present at much higher concentrations than nitrogen dioxide in non-polluted locations.

The use of sodium carbonate scrubber tubes in front of the gold tubes was found to reduce hydrogen sulfide losses to 10% or less for 20-30 minute sampling periods in the presence of 100 ppb ozone. Sodium carbonate scrubber tubes were prepared by treating acid washed Anakrom-C22 with a 5% Na_2CO_3 in water solution. Absorbent beds were tubular 2.5 cm long and 1.4 cm in diameter. All scrubbers were conditioned by passing H_2S from a permeation tube standard through them for a short time. Scrubber beds absorb 1-2 ng of H_2S in this treatment and do not absorb any more H_2S or DMS in operation.

Glass fiber filters (Gelman A), when treated with 10% sodium carbonate solution and then dried were found to be similarly effective in oxidant removal. The advantages of the filters are easy preparation and very little pressure drop in

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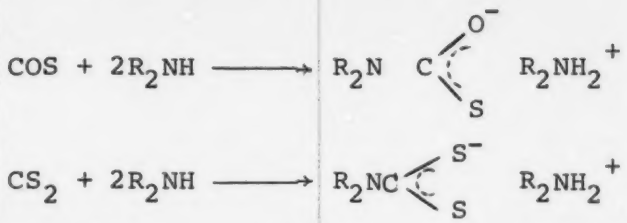
sampling, and no conditioning requirement. They have been used in sampling ocean air containing 5 parts per trillion (ppt) sulfur.

PRECONCENTRATION OF COS AND CS_2 BY SECONDARY AMINES

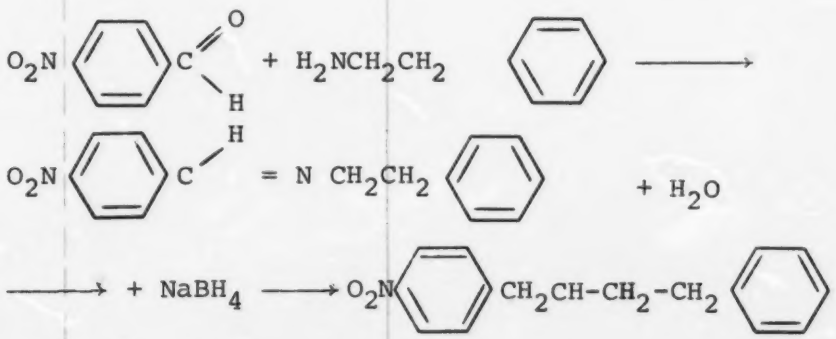
Carbonyl sulfide and carbon disulfide form thiocarbamates with secondary amines.



The resulting compounds are decomposed to produce the reactants by heat or acid treatment. The COS compound is more readily decomposed.

The preparation of several high molecular weight secondary amines was carried out in an attempt to obtain a thermally stable solid which could be used in preconcentration. Condensation reactions of aromatic aldehydes with primary amines followed by reduction with sodium borohydride was the general reaction approach used.

A typical reaction sequence is



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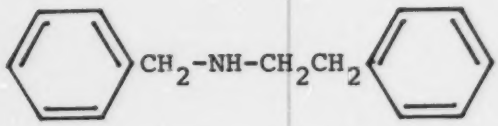
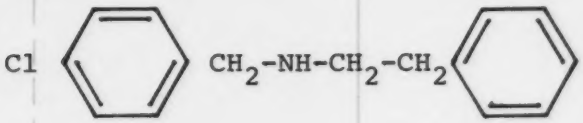
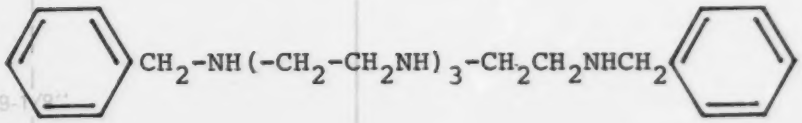
Compounds prepared and tested for use include the following

a) 

b) 

c)

d) 

e) Tetraethylenepentamine derivative of chloromethylated polystyrene, 1% divinylbenzene copolymer (8).

Compounds shown above deposited on solid surfaces and packed into sampling tubes all absorbed COS and CS_2 from low concentration air streams. Carbonyl sulfide was removed by simply heating the compounds to 110-120°C. Carbon disulfide was not removed by this treatment. At temperatures above 140-150° compounds a, b, and c sublimed. Compounds d and e melted and partly decomposed. Decomposition or sublimation of the organic compounds, of course, rendered impractical recovery and multiple reuse of the organic absorption tubes.

A condensation reaction of tetraethylenepentamine and toluene-2,4-diisocyanate was also carried out according to a published method (9). The product, also a polymer and a secondary amine, was not effective in absorbing COS or CS_2.

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GOLD FOIL PRECONCENTRATION

Because of the low recoveries of H_2S occasionally noted when using Au coated sand, a systematic survey was initiated to determine which part of the preconcentration tube was responsible. Four sampling tubes were prepared, one each containing gold coated silica (sand) quartz, wool only and uncoated silica support.

An initial comparison of the relative response of each towards a derivatized H_2S sample showed that the Au foil tube gave 50% higher response than the Au coated sand. After repeatedly washing with concentrated HCl and processing several H_2S derivatized samples, the response of the gold coated sand increased to better than 90% of the foil tube. One foil tube was tested periodically over several months. Its response did not change. Presumably the problem with sand supported gold is related to trace iron or nitrates making their way to the surface and thus causing interference which is removed by acid washing.

Because of the better response of the gold foil tubes several were prepared and used in subsequent experiments. The detection system was recalibrated using a gold foil tube as the preconcentration standard tube. The resulting calibration curves had less point scatter than previous curves using the gold coated sand tubes, especially for small sample sizes in the 0.5-10 ng range.

The comparative response of sand supported gold and gold foil tubes to several sulfur compounds was studied with the results shown in Table 1. Loss of sample relative to the foil tube was found for the gold sand tube. Particularly large losses were noted for COS and the mercaptans. Analyses of a second gold foil tube used as a back-up tube, see Table 2, showed that this loss was not due to inefficient adsorption by the gold sand. Further examination of the data for the quartz wool and sand tubes indicates that the loss is attributable to the silica and quartz wool surfaces, since these tubes did not allow all of the COS and mercaptans to pass. Additionally, partial oxidation

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of these compounds to SO_2 occurred and this SO_2 was found both on the quartz wool and silica tubes and on the foil back-up tube.

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TABLE 1. SULFUR COMPOUND RECOVERY EFFICIENCIES OF SORPTION TUBES

(Percent Recovered)

Compound	Au Foil	Au Sand	Quartz Wool	QW/sand 60/80 mesh	QW Coarse Sand
H_2S[a]	100	50-80	——	——	0
COS[a]	100	5	0[b]	0	0
CS_2[a]	100	20	0[b]	0[b]	——
SO_2	100	0	90	80	——
DMS	100	95-100	0	0	——
PrSH	100	50	0	0	——

[a] Recovered as diethyl sulfide [b] SO_2 recovered

TABLE 2. SULFUR COMPOUND RECOVERY BY SECOND GOLD TUBE

Compound	Au Foil	Au Sand	Quartz Wool	QW/Sand
H_2S	<1%		~70%	
COS	<1%	~5%	>90%	>90%
CS_2	<1%	~5%		
SO_2	ND	ND	~20%	~10%
DMS	ND	ND	>95	>95
PrSH	ND	ND	80[a]	~40

[a] SO_2 peak also found ND - not detected

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Dimethyl sulfide seems to be quite stable towards oxidation loss of sample. Both the gold foil and gold sand tubes exhibited good scrubbing and recovery efficiencies. No DMS was detected on the quartz wool and silica tubes and essentially all of the DMS was observed to pass.

The observed performance of the gold/sand tubes can be explained by the combination and variety of reactions possible. One would expect good scrubbing performance due to the presence of gold, which can scrub all sulfur compounds except SF_6. This is observed experimentally. Analysis should yield some sample loss due to the oxidation of certain sulfur compounds before contact with the gold surface. this is also observed experimentally. Occasionally an SO_2 peak is observed as SO_2 desorbing from the gold sand. This would be consistent with the results if the gold present becomes saturated with SO_2. After saturation the SO_2 would be absorbed by the silica. This could then be desorbed as SO_2. Apparently until saturation occurs, the gold/silica combination can cause slow oxidation of SO_2 to sulfate which then cannot be recovered as SO_2 by nitrogen desorption.

Quartz wool plugs were placed in front of a gold foil to hold it in position. The first 2 standards of H_2S tried gave full response, but the third was cut to ≈ 40%. Several other standards gave response variable from 40-80%. The quartz wool was removed and a follow up standard gave full response. Because quartz wool causes a loss of sample, sampling tubes currently in use contain nothing but a rolled up piece of gold foil approximately 3 cm x 4 cm in size.

If care is taken when using the sand tubes, and standards are checked frequently, they may be used and will give reproducible and satisfactory results. A calculated loss of sample must be accepted in this case along with a reduction in precision.

Gold foil tubes under ambient sampling conditions have given reproducible results. Standards checked on the foil tubes following field use have consistently been on the calibration curve showing outside use does not degrade the tubes. After about

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eight months and approximately 500 analyses one original Au foil tube showed a decrease in recovery of about 15%. The foil was removed and placed in a new quartz holding tube. The response returned to normal. Microscopic examination of the now somewhat cloudy original quartz holding tube showed that the surface had become etched. It is believed that the vastly increased surface area due to the etching caused partial loss of the sample in a mechanism similar to that observed for the silica tube.

A set of three gold foil tubes were used for 15 samples of H_2S of 4.0 ng. each. The repeatability of analyses is 4.5% r.s.d. This rises to approximately 8% near the detection limit. The detection limit at 2 x RMS noise for H_2S using the foil tube is 0.115 ng H_2S as H_2S. For DMS it is 0.33 ng as DMS.

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SECTION 4

CEDAR ISLAND FIELD WORK

Cedar Island, North Carolina is a site having a large salt marsh. Air analyses at that location during the summer of 1977 indicated that substantial amounts of H_2S and DMS were present. This prior work (3) was done using a less specific method than the one used here. In addition, the earlier analysis procedure did not provide SO_2 data.

It was decided to repeat analyses at the Cedar Island site to compare with the prior year's work and in addition to analyze for sulfur compounds at a wider range of locations. This field work also had as an objective the evaluation of the method in field use.

Two sulfur analyzers, sampling equipment, and calibration equipment were transported to the field laboratory site at Cedar Island, North Carolina. Analysis equipment was set up, rechecked for calibration and put into operation. The analysis equipment was of the type shown in Figure 2. Premeation tubes were used to calibrate for H_2S, DMS and SO_2. Samples were preconcentrated after filtering using sampling tubes of the type shown in Figure 1. Tubes protected by sodium carbonate scrubbers were used on several miscellaneous samples and compared to samples collected without scrubbers. There appeared to be little difference in the analyses and consequently scrubbers were not used for most work.

Sampling tubes were attached by clamps to 10 meter high masts and air was sampled for periods of 15 to 30 minutes. The samples were removed, sealed with Parafilm and returned to the laboratory where they were immediately analyzed.

Several types of field sampling were to be performed;

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diurnal variation, vertical profiles of sulfur concentration and simply a collection of ambient concentration analyses from various locations. Results of analyses are detailed in the following sections.

DIURNAL VARIATION STUDY

A number of factors may be involved in the production of H_2S, DMS and SO_2 in the Cedar Island location. Among the likely influences are; photosynthetic activity, temperature, tidal variation, and precipitation. Although it is not easy to separate these effects, it was decided nevertheless, to carry out a study of sulfur compound concentration variations over a 36 hour to 48 hour period.

This was done with samples taken at a height of 2 meters in duplicate in the mowed grass field near the field laboratory. Samples were taken at one to three hour intervals and analyzed immediately. Sample sizes ranged from 27 to 38 liters in volume, taken in 15 minute sampling periods. The series was terminated after 1400 hrs. of the second day because of squally, unsettled weather.

Numerical analytical results are given in Table 3. The variations in H_2S, SO_2, DMS and COS are shown in Figures 5, 6, 7 and 8.

The salient feature is the decrease in SO_2 and H_2S over periods of decreased sunlight. This is not unexpected since the biogenic production of H_2S is known to be photosynthetic. Sulfur dioxide, the product of H_2S oxidation, should follow H_2S production and appears to do so. The data given in Table 3 and the figures are not the only ones taken showing a light-darkness effect on H_2S and SO_2. A comparison of vertical profiles taken at the Day's ditch location (see Figures 11 and 12) at noon versus at sunset also show that H_2S and SO_2 are decreased substantially near sunset.

DMS appears to show a cycle with a relative increase at night and possibly a release from soil after the dew had evap-

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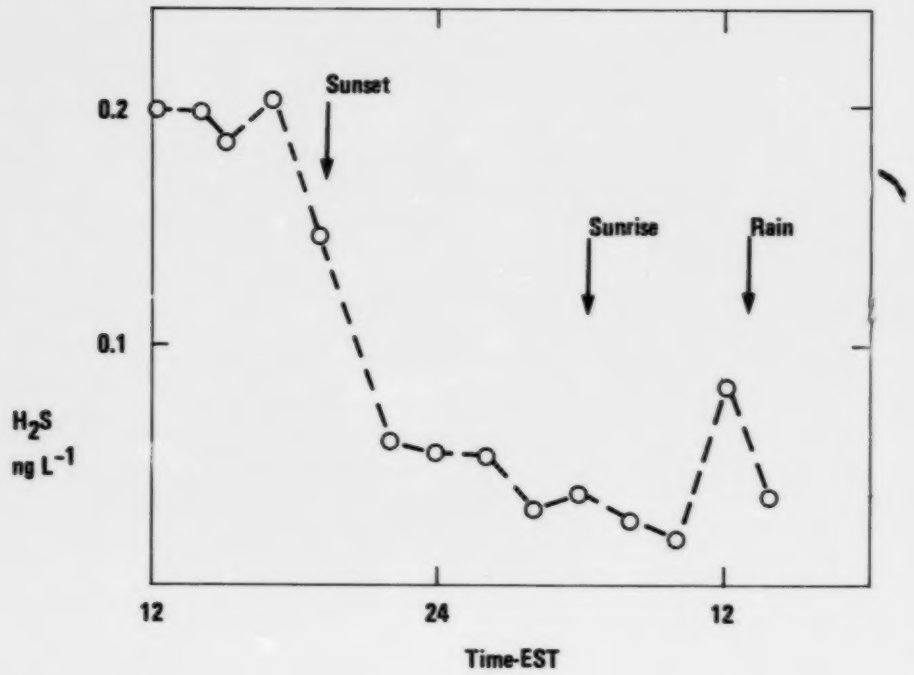

Figure 5. Diurnal variation of H_2S

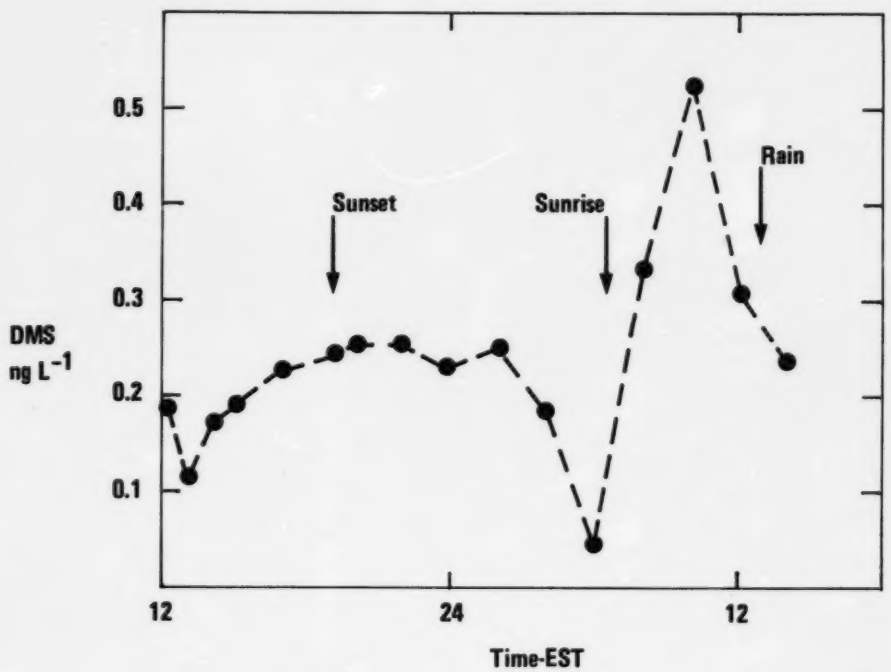

Figure 6. Diurnal variation of DMS

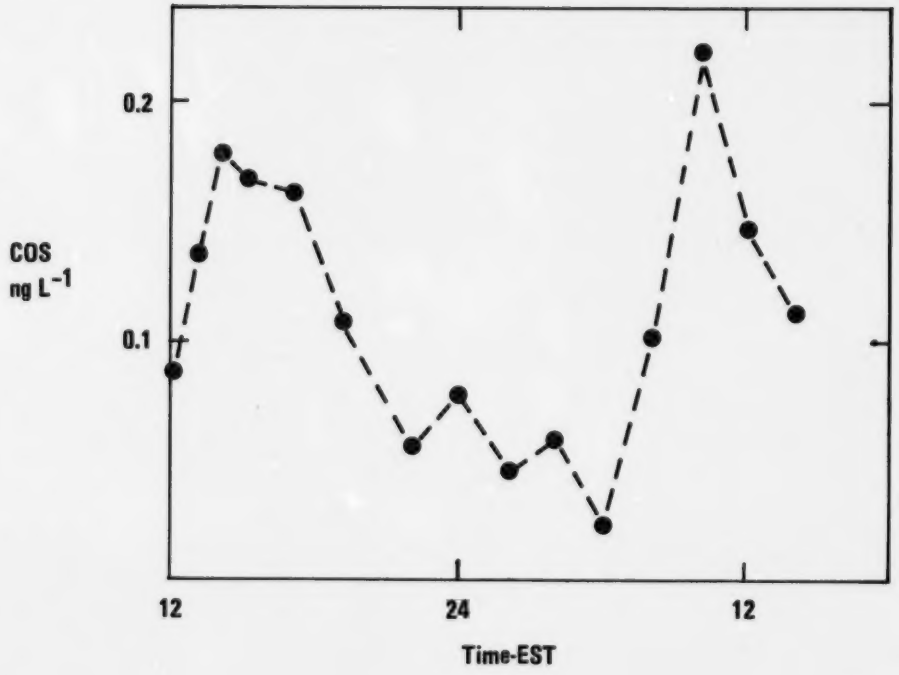

Figure 7. Diurnal variation of COS

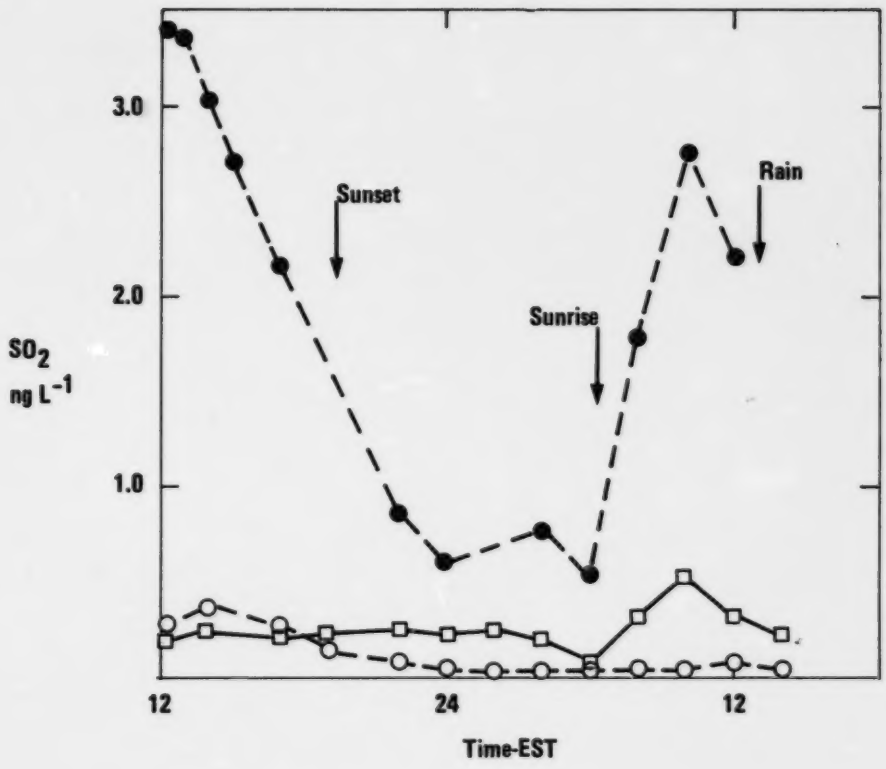

Figure 8. Diurnal variation of SO_2

TABLE 3. DIURNAL VARIATION STUDY, AUGUST 4-5, 1978
($ng\ L^{-1}$)[b]

Time	COS[a]	H_2S	DMS	SO_2	Remarks
1200	0.086	0.20	0.19	3.4	Wind - 120-135°, 5-6 mph
1300	0.14	0.14	0.11	3.4	Wind - 130-140°, 5 mph
1400	0.18	0.20	0.17	3.0	Wind - 135°, 5 mph
1500	0.17	0.19	0.19	2.7	Wind - 135°, 5 mph
1700	0.16	0.21	0.23	2.2	Wind - 135°, 4-5 mph, 29.5°C
1900	0.11	0.15	0.24	2.6	Wind - 135°, 3 mph, 28.5°C
2200	0.056	0.065	0.25	0.86	Wind - 120°, 2 mph, 28.0°C
2400	0.078	0.056	0.23	0.61	Wind - 125°, 2 mph, 27.5°C
0200	0.045	0.054	0.25	1.5	Wind - 128°, 0-2 mph, 26.5°C
0400	0.059	0.031	0.10	0.82	Wind - variable, 0-2 mph, 27°C
0600	0.022	0.039	0.10	0.52	Wind - 130°, 0-5 mph
0800	0.10	0.026	0.33	1.8	Wind - 120-135°, 6 mph, 28.5°C
1000	0.22	0.019	0.53	2.8	Wind - 120°, 6 mph
1200	0.15	0.082	0.31	2.2	Wind - 135°, 6 mph, rain nearby
1400	0.11	0.037	0.24	---	After rain

[a] Calculated using the H_2S calibration curve

[b] Samples were approximately 27 liters each collected in 15 minute periods

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orated in the morning. This increase in DMS while H_2S decreases during the night hours is also reflected in the higher DMS concentrations shown in Tower C and Tower B, both taken at night.

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VERTICAL SAMPLING STUDIES - BLOCKHOUSE AREA

Two different sets of samples were taken from towers at night, one from 0.2 to 12 m and another 0.2 to 10 m. Analysis data are given in Tables 4 and 5 with data plotted in Figures 9 and 10. The sampling location was an open field with short, mowed lawn grass surrounded by a 2 m high chain link fence. The first sample set, Tower B, was taken at a point much closer to the fence than the second set at Tower C.

In both cases the night effect on the DMS - H_2S ratio can be seen with DMS being higher in both cases than H_2S.

The ground emission of DMS, H_2S and SO_2 is observed. DMS in both cases decreases generally with height indicating a ground source. Profiles for H_2S and SO_2 in the second set and H_2S in the first set indicate some contribution from a more distant source.

The increase in SO_2 and H_2S concentrations above a minimum near 2 m agree with the prior year's experience with vertical profiles taken at the same location. This could be attributed to an on-shore breeze from Pamlico Sound mixing with an air mass of much higher SO_2 concentration from the nearby salt marshes.

DAY'S DITCH STUDIES

Two vertical profiles were obtained at a location some 2 km from open sea water in a salt marsh. No obstructions of any kind were present above the marsh grass and upwind of the sampling location. One sample set was taken at noon and another just before sunset. Analysis data are given in Table 6 and plotted in Figures 11 and 12.

The set taken near sunset had much lower H_2S and SO_2 concentrations reflecting a much decreased emission of both. This agrees with the diurnal variation study experience.

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TABLE 4. TOWER B VERTICAL PROFILE (ng L^{-1})

Height, meters	H_2S	DMS
12	1.50	0.081
7.5	1.38	0.14
5	0.71	0.16
3	1.13	0.14
2	1.24	0.14
1	0.90	0.093
0.7	1.0	0.17
0.5	1.47	0.18
0.2	1.58	0.18

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Samples were taken at 2130 hrs. August 5, 1978, at the blockhouse location. Sample volumes were approximately 30 L taken over a 15 minute period.
Wind: 135°, 5 mph, 28°C.
SO_2 was removed by carbonate scrubbers during sampling

TABLE 5. TOWER C VERTICAL PROFILE (ng L^{-1})

Height	H_2S	DMS	SO_2
10M	0.11	0.22	1.24
5M	0.087	0.32	0.77
2M	0.085	0.32	0.63
1M	0.029	0.33	0.77
0.5M	0.066	0.40	0.97
0.2M	0.12	0.29	1.66

Samples were taken at 2120 hrs. August 8, 1978 in the field at the blockhouse location. Sample volumes were from 50-66 L taken over a 30.5 minute period. Wind: 190°, 2-3 mph; RH 75%, 27.2°C.

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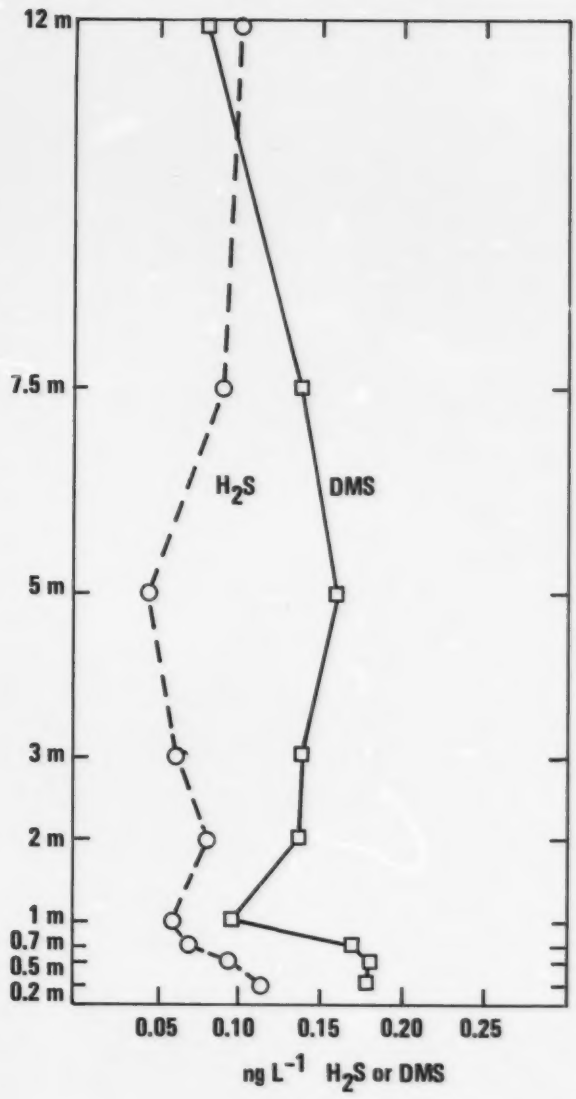

Figure 9. Vertical distribution of sulfur compounds, Tower B, Night, Grass Field

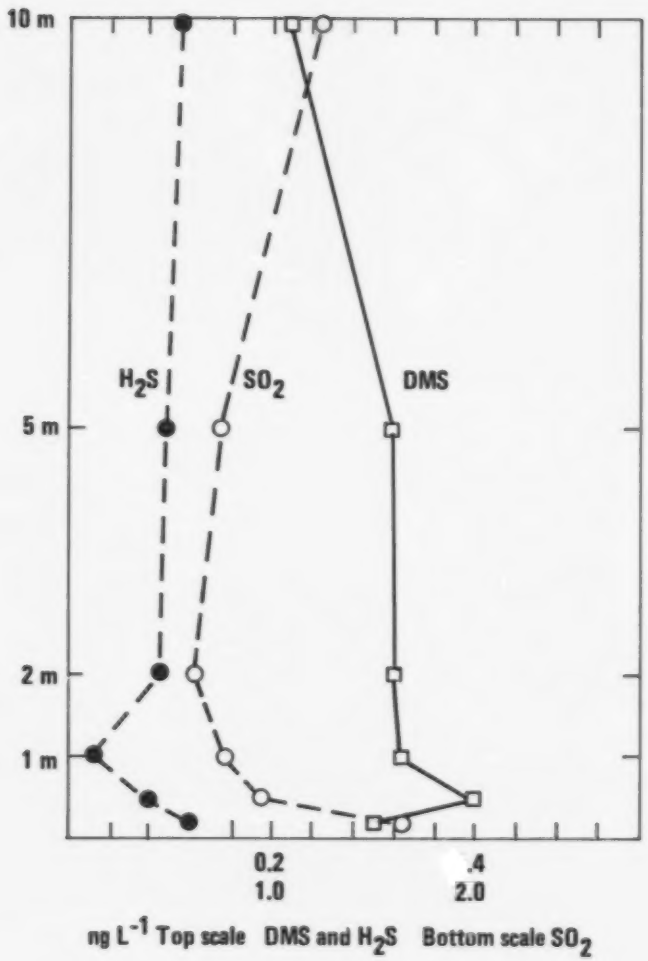

Figure 10. Vertical distribution of sulfur compounds, Tower C, Daytime, Grass Field

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TABLE 6. DAY'S DITCH VERTICAL PROFILES

A. Noon Sample Set(ng L^{-1})

Height, meters	H_2S	DMS	SO_2
10	0.67	0.11	3.4
5	0.89	0.22	3.1
2	0.50		3.4
1	0.96	0.11	3.9
0.5	2.1	0.12	5.0
0.2	2.4	0.21	4.8

Samples were taken at 1215 hrs. August 7, 1978 at the salt marsh location next to Day's Ditch, Cedar Island, N.C. Sample volumes ranged from 23-36 L taken over a fifteen minute period.
Wind: 190°, 2-3 mph, 35°C.

B. Sunset Sample Set(ng L^{-1})

Height, meters	H_2S	DMS	SO_2
10	0.20	0.26	2.0
5	0.19	0.30	1.6
2	0.15	0.48	2.1
1	0.20	0.53	2.3
0.5	0.38	0.52	2.4
0.2	0.25	0.78	1.9

Samples were taken at 1930 hrs. just prior to sunset, August 7, 1978 at the salt marsh location next to Day's Ditch, Cedar Island, N.C. Sample volumes ranged from 24 to 36 L taken over a 15 minute period.
Wind: 190°, 5-6 mph, 28°C.

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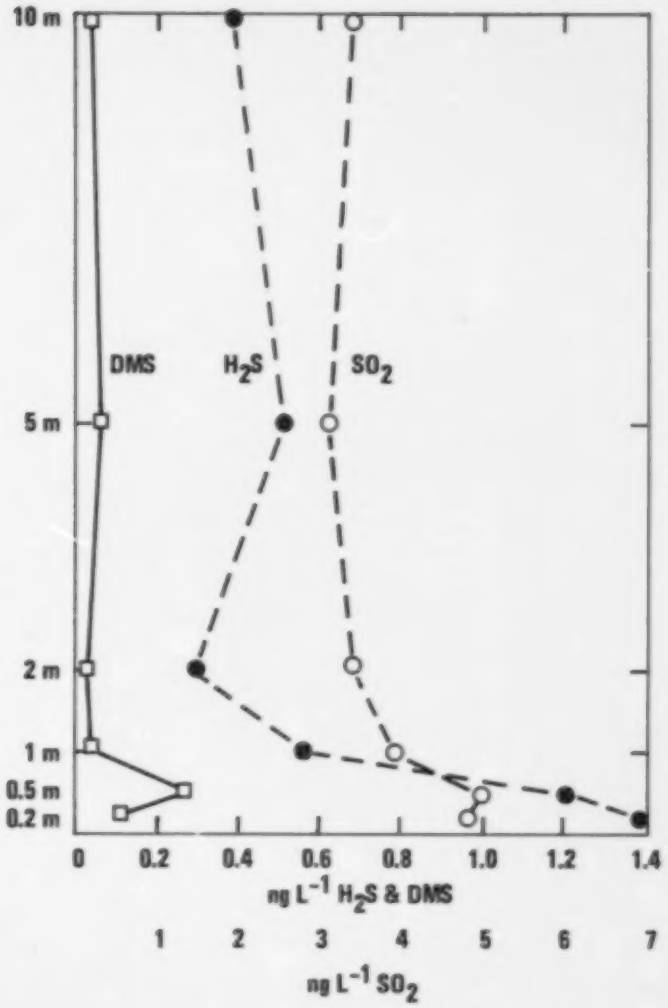

Figure 11. Vertical distribution of sulfur compounds, Day's Ditch, Noon

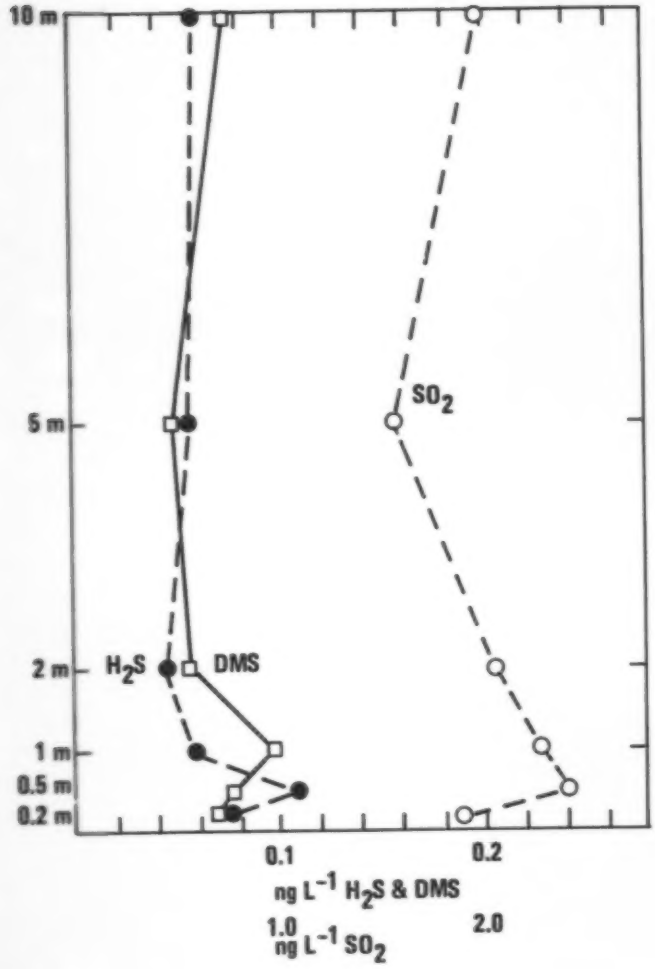

Figure 12. Vertical distribution of sulfur compounds, Day's Ditch, Sunset

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A marked increase in H_2S and DMS and SO_2 concentration occurs from 2 m to 0.2 m especially for the noon sample data set. Since the marsh grass was approximately 0.75 m high it would tend to substantially influence the air mass below 2 m. Grass should reduce air mixing and so sulfur gases should build up in concentration in the air below the grass top.

MISCELLANEOUS SAMPLES

A number of samples were taken during the field sampling studies at the Cedar Island site.

Analytical data are given in Table 7. The first 5 analyses taken over a 7 hour period shows a marked increase in DMS concentration as a function of time of day. The H_2S concentration did not decrease as expected with nightfall.

TABLE 7. MISCELLANEOUS ANALYSES (ng L^{-1})

Sample Description	H_2S	DMS
Air, 2M, 1530 hrs, 8-3-78, wind 160°, 6 mph, 30.5°C	0.12	<0.05
Air, 2M, 1750 hrs. 8-3-78	0.088	<0.05
Air, 2M, 1800 hrs. 8-3-78	0.069	<0.05
Air, 2M, 2125 hrs. 8-3-78	0.12	0.15
*Air, 2M, 2230 hrs.	0.12	0.66
Chamber Sample - 1 0.5 L	15.6	64.2
Chamber Sample - 2 0.5 L	42.6	24.6
Chamber Sample - 3 0.5 L	22.4	31.7

*SO_2 1.4 ng L^{-1} SO_2 was removed from all other samples

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VERTICAL DISTRIBUTION OF COS

After identification of the initial peak in all chromatograms as COS, it was decided to re-analyze all charts for data on COS. This was done using the H_2S calibration curve for COS response. Data from the diurnal variation study are shown in Figure 7. Vertical distribution data of COS for three of the tower sets is given in Table 8 and plotted in Figure 13.

The salient features of the data are that (1) COS emission is increased during the day and that (2) the ground appears to be a source as evidenced by the Day's Ditch-noon set.

TABLE 8. COS VERTICAL DISTRIBUTIONS (ng L^{-1} as H_2S)

Height, meters	Day's Ditch-1	Day's Ditch-2	Tower C
10	0.30	0.13	0.12
5	----	0.075	0.062
2	0.28	0.089	0.12
1	0.38	0.15	0.13
0.5	0.64	0.12	0.087
0.2	0.50	0.11	0.10

See Tables 3 and 4 for sampling conditions

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SECTION 5

PRAIRIE VIEW, TEXAS FIELD WORK

INTRODUCTION

Prairie View, Texas is situated approximately 45 miles W NW of Houston, Texas and is approximately 75 miles from the highly industrial area of Galveston Bay. This location had been selected as one at which substantial deposition of sulfur compounds from the air could be observed. Priarie View is the location of the University of Prairie View, a school having a strong program in agriculture.

Several U.S. EPA contractors were engaged in dry deposition studies and air analyses at the location. The actual site at which deposition was to be studied was a large open field, grass covered and having a long open area upwind of the sampling location. The location was selected for its long wind fetch, meterologically favorable to dry deposition studies. A large cattle herd was grazing in the field.

One of the objectives of this study was to compare vertical distribution data using the preconcentration tube method to other data obtained in dry deposition studies. Other objectives were essentially the same as for the Cedar Island site study, to determine the distribution of sulfur compounds present and to evaluate the method in field use.

Actual field work included set-up of the sulfur analysis equipment, recalibration and analyses. The main effort went into determining the vertical distribution of sulfur compound concentrations.

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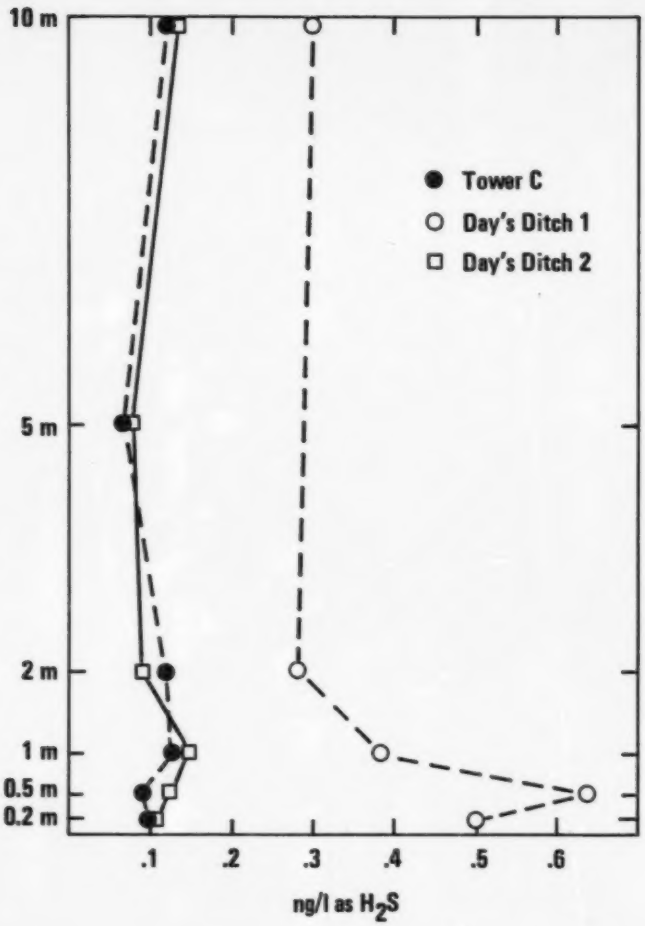

Figure 13. Vertical distribution of COS

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MISCELLANEOUS SAMPLES - PRAIRIE VIEW

Several air analyses were obtained during the several days required for set-up of the analysis equipment and calibration. One partial vertical distribution was obtained. The analytical results are given in Table 9.

Samples were taken near a sorghum crop field at the field laboratory site and also near some cattle pasture fields. Prevailing winds were generally from the direction of the crop field and so reflect the emissions from that area. Note that the cattle field area air sample was high in both H_2S and SO_2.

These analyses were taken at a location some 1000 meters south of the dry deposition study field rather than at that location for two reasons. One was to avoid the effect of a large cattle herd on sulfur analyses and the other was to obtain data on a crop field emission.

Several analyses other than given in Table 9 were made during daylight hours to assess SO_2 and total sulfur compound concentrations. Results were quite variable but total sulfur ranged from 102 ngL^{-1} to 10-12 ngL^{-1} over several days. This was quite in agreement with the experience of others doing sulfur analyses at the location.

VERTICAL DISTRIBUTION - SORGHUM FIELD LOCATION

Vertical distributions of sulfur compounds were obtained partly as preparation for the work at the dry deposition site and partly to have data at a field location not having cattle present. Data on one partial vertical distribution is given in Table 9. Two vertical distribution data sets are given in Tables 10 and 11. Data are plotted in Figures 14 and 15.

Analyses below 2 m are scattered and probably show the effect of foliage on wind turbulence. This is the same as observed in most vertical distribution experiments.

Also notable is the contrast between studies 1 and 2. The latter was observed after a large change in wind direction. For several days the wind direction had been from the S.E., the

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TABLE 9. MISCELLANEOUS SAMPLES - PRAIRIE VIEW (ng L^{-1})

Time	Location	H_2S	DMS	SO_2
021 hrs 8-24-78	Near Sorghum field	0.045	0.026	0.26
0045 hrs 8-24-78	Near Sorghum field	0.073	0.34	0.50
2145 hrs 8-24-78	Near Cattle yard	0.56	0.20	high
2140 hrs	In Sorghum field			
	2.0 m	0.045	0.080	0.20
	1.0 m	0.080	0.089	0.53
	0.5 m	0.047	0.067	0.45
	0.2 m	0.085	0.10	0.16

TABLE 10. SORGHUM FIELD VERTICAL DISTRIBUTION (ng L^{-1})

Height, meters	H_2S	DMS	SO_2
10	0.073	0.22	0.49
5	0.044	0.21	0.47
2	0.063	0.21	0.49
1	0.18	0.14	0.27
0.5	-low-	0.21	0.19
0.2	0.044	0.23	0.23

Note: 26 Aug. 78, 2200 hrs., 80°F, RH 65%, wind - N 130°, 0-4 mph

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TABLE 11. SORGHUM FIELD VERTICAL DISTRIBUTION 2 (ng L^{-1})

Height, meters	H_2S	DMS	SO_2
10	0.098	0.11	0.099
5	0.12	0.10	0.11
2	0.21	0.17	0.72
1	0.056	0.089	0.63
0.5	0.11	0.11	0.67
0.2	0.31	0.12	1.2

Note: 28 Aug. 78, 1530 hrs., 80°F, RH 42%
wind N.E., canopy 6 mph, middle air 11 mph
upper air (10 m) 15 mph

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direction of the Houston industrial area. Several hours prior to the sorghum field study 2, there was a shift in wind direction to the north. A slight rain shower occurred during the night just prior to taking the vertical distribution set 2. The SO_2 in the upper air decreased substantially from concentrations nearer the ground remained high. This may have been simply the desorption of SO_2 from the foliage or the ground.

Dimethyl sulfide appears to be a substantial constituent of the sulfur compounds. It is higher than H_2S generally during the night.

None of the sulfur compounds are as high in content in air as observed at the Cedar Island, N.C., location.

PASTURE FIELD VERTICAL DISTRIBUTION SETS

Four simultaneous tower sets were obtained at the dry depostion study location at Prairie View. Towers were 200 ft. separated and normal to the wind direction. Analytical data are

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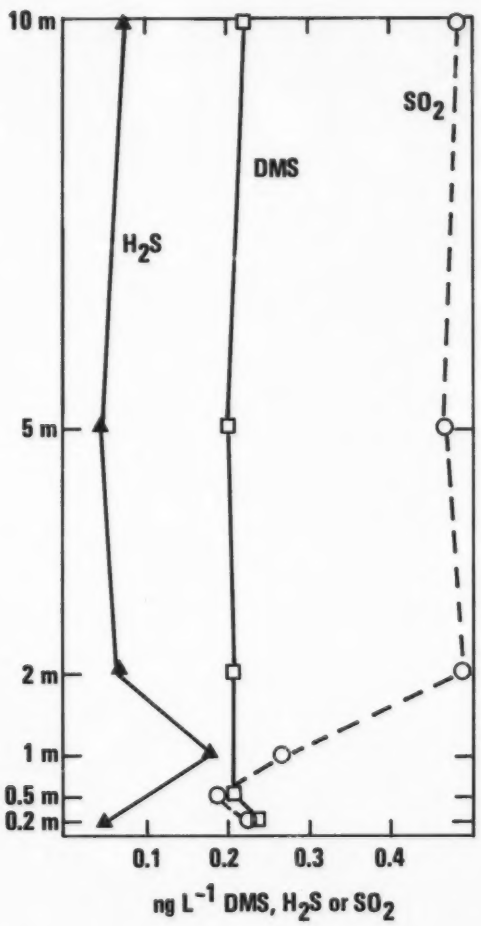

Figure 14. Sorghum field vertical distribution 1

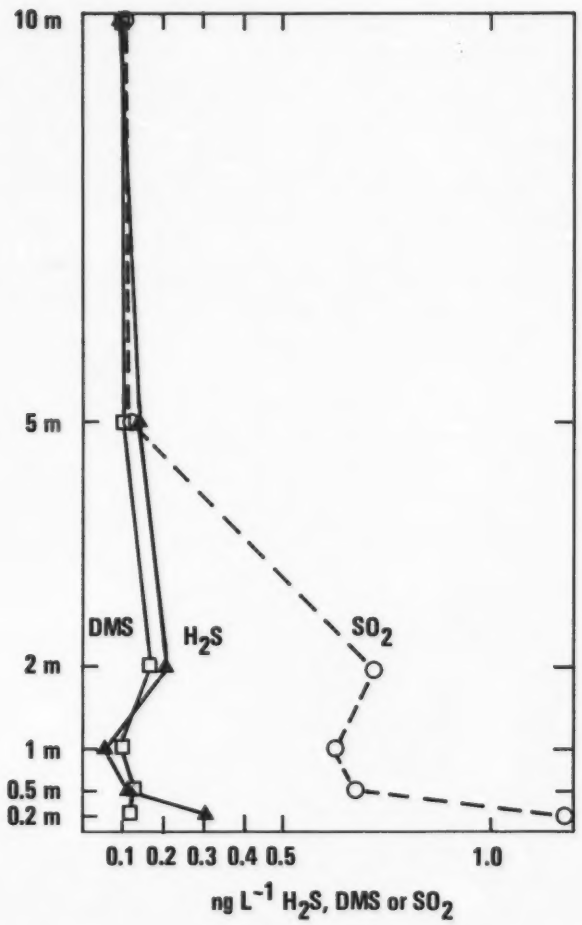

Figure 15. Sorghum field vertical distribution 2

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given in Table 12.

Two sets, Towers 1 and 3 were obtained using preconcentration without sodium carbonate scrubbing tubes. Tower sets 2 and 4 were done with sodium carbonate scrubbing tubes.

Comparison of all four sets shows that the sodium carbonate scrubbers also removed substantial amounts of H_2S and DMS despite their prior use and thus conditioning. It is apparent that data from Towers 2 and 4 are low.

The vertical distributions of sulfur compounds for the Tower 1 and 3 sets are shown in Figures 16a and 16b. There is some indication that DMS is higher in concentration near the ground but little evidence that H_2S and SO_2 show any such gradient.

Sulfur dioxide was far higher in concentration than any of the sample taken at the sorghum field location.

Both H_2S and DMS appeared to have approximately the same concentration at the pasture field as at the sorghum field site.

TABLE 12. DRY DEPOSITION STUDY SITE VERTICAL DISTRIBUTION SETS

TOWER 1 ($ng\ L^{-1}$)			
Height, meters	H_2S	DMS	SO_2
10	0.074	0.05	8.3
5	0.11	0.14	10.7
2	0.074	0.26	9.2
1	0.13	0.14	8.8
0.5	0.076	0.20	7.6
0.2	0.042	0.34	10.1

Note: 27 August 1979, 1700 hrs., 91°F, RH 58%, wind 122° Azimuth, 8-11 mph at 2 m.

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TABLE 12 (continued)

TOWER 2 (ng L^{-1})

Height, meters	H_2S	DMS
10	0.029	tr.
5	0.024	0.03
2	0.021	0.07
1	0.023	tr.
0.5	0.053	tr.
0.2	0.17	0.08

TOWER 3 (ng L^{-1})

Height, meters	H_2S	DMS	SO_2
10	0.043	0.23	11.9
5	0.025	0.24	11.5
2	0.17	0.39	11.4
1	0.27	----	----
0.5	0.13	0.72	9.9
0.2	0.09	0.24	12.5

TOWER 4 (ng L^{-1})

Height, meters	H_2S	DMS
10	0.008	tr.
5	0.014	0.032
2	0.038	0.040
1	0.026	0.019
0.5	0.032	0.072
0.2	0.013	0.049

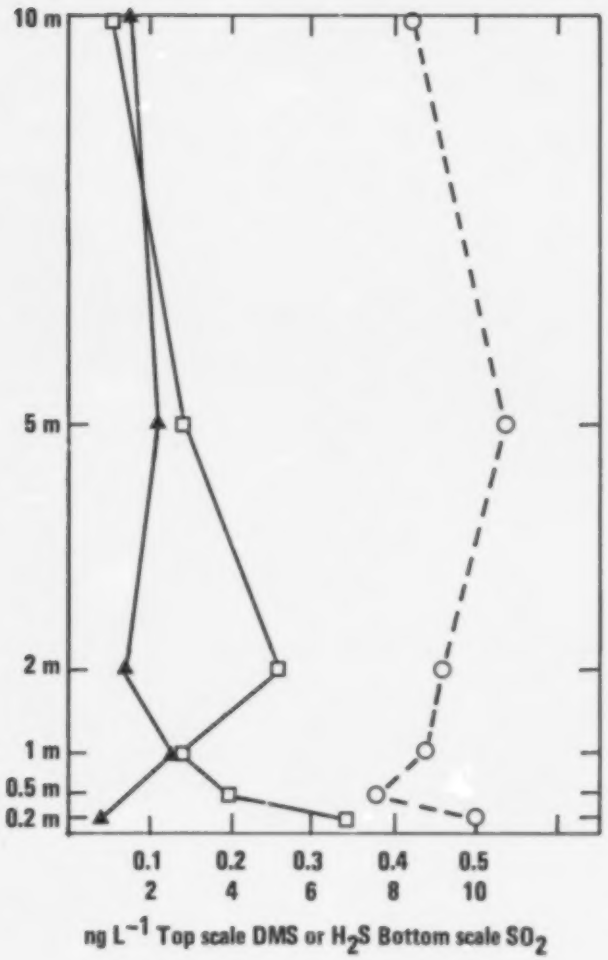

Figure 16a. Dry deposition site vertical distributions

Tower 1

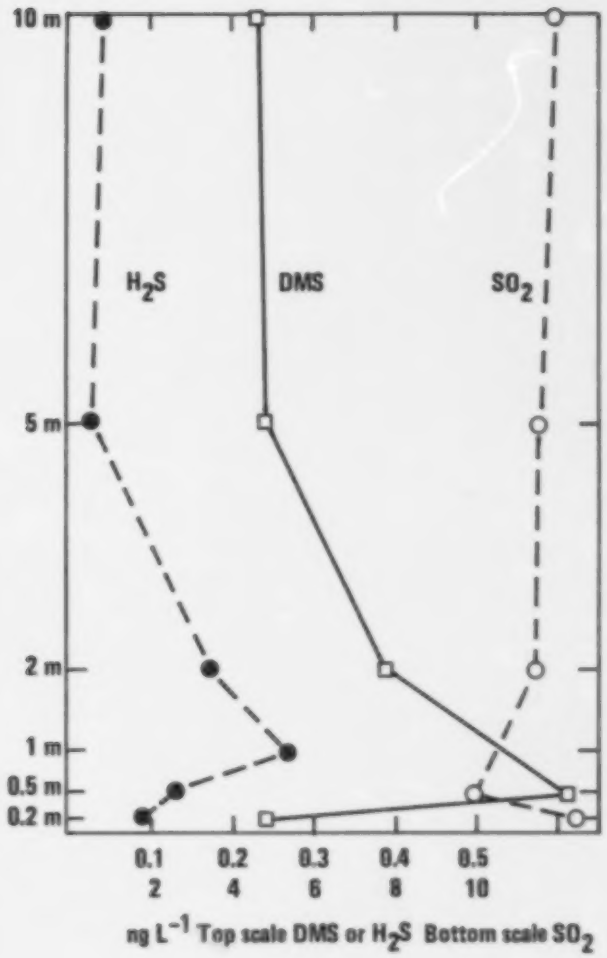

Figure 16b. Dry deposition site vertical distributions, Tower 3

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